CHAPTER V

DISCUSSIONS
5.1 STUDIES IN IODINE SOLUTION IN DIFFERENT SOLVENTS

5.11 Effect of Iodine Concentration on the Organic Yield of Solvent

It has been observed that the organic yield in pure solvent increases with decrease in the concentration of iodine (Table 1a). Unak et al.\textsuperscript{161} however, observed much lower organic yield of 2.12\% when they irradiated liquid and gaseous solution of iodine in benzene for $10^{-4}$ M to $10^{-2}$ M concentration range.

The mechanism for such behaviour can be explained on the basis of model proposed by various authors for the recoil reactions of iodine with methane\textsuperscript{162}, ethylene\textsuperscript{163} and butane\textsuperscript{164}. They suggested that after the (n-\gamma) recoil majority
of recoil iodine atoms exist as positively charged iodine ions of magnitude ranging from 1 to 9. These charged iodine ions can react with solvents by electrophilic attack, to give an organic yield. When recoil iodine ions interact with its own molecule, there would be a loss of energy and recoil iodine ion would end up as a thermolised iodine atom. The probability of this process would be more with higher iodine concentration. Thus there would be a decrease in organic yield with concentrated solution. On the other hand, with dilute solution, cage effect due to large number of molecular fragments of solvent molecule, will dominate, which would increase the organic yield of solvent in dilute solution. This has been observed in the present experiment (Table 1a).

5.2 EFFECT OF DIFFERENT SOLVENTS ON ORGANIC YIELD OF SOLVENTS IN IODINE SOLUTIONS

The organic yield of solvents in benzene and toluene is more or less constant (20 to 25%) except for 10⁻⁴ M solutions. Whereas it is slightly higher in nitrobenzene and ortho-nitrotoluene (24 to 36%). This behaviour can be explained by similar argument, as stated earlier. The electrophilic type reaction of positively charged iodine atoms with benzene and toluene is expected to be approximately same, because molecules of both solvents have nearly the same π-electron density on the benzene ring. But in other
two solvents (nitrobenzene and ortho-nitrotoluene) though have less electron cloud for electrophilic substitution, they would have stronger intermolecular force which is exhibited by their higher boiling points (i.e. the boiling points of nitrobenzene - 210°C and ortho-nitrotoluene - 220°C are much higher than that of benzene 80°C and toluene 110°C). Thus nitrobenzene and ortho-nitrotoluene would give a better cage effect, thus increase its organic yield. Further more these nitrosubstituted solvents would also have nucleophilic reaction with negatively charged iodine ions. Both these effects would increase the total organic yield for these two solvents.

5.3 STUDIES IN SOLUTIONS OF COMPOUNDS IN DIFFERENT SOLVENTS

5.31 Effect of Concentration of Compound on the Organic Yield of Solutions and Solutes

For every compound (OINB, PINB, 24-DNIB, PIANLN and PIPHNL) the organic yield of solutions remains almost constant for various concentrations of solute in a given solvent; but is different for different compound in different solvents. It is also observed (Table 23) that for 10⁻¹ M concentration the organic yield of solution of all compounds in different solvents follows a trend where Benzene < Toluene < Nitrobenzene < ortho-Nitrotoluene. Similar trend has been observed with
<table>
<thead>
<tr>
<th>Observation No.</th>
<th>Compound</th>
<th>SOLVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzene</td>
</tr>
<tr>
<td>1</td>
<td>OINB</td>
<td>30.18</td>
</tr>
<tr>
<td>2</td>
<td>PINB</td>
<td>28.51</td>
</tr>
<tr>
<td>3</td>
<td>24-DNIB</td>
<td>28.5</td>
</tr>
<tr>
<td>4</td>
<td>PIANLN</td>
<td>34.58</td>
</tr>
<tr>
<td>5</td>
<td>PIPHNL</td>
<td>37.34</td>
</tr>
</tbody>
</table>
iodine solutions also (Table 1a) and results can similarly be explained on the basis of the intermolecular forces for these solvents.

It is further observed that the organic yield of solute decreases with decrease in the concentration of compound in all solvents (Table nos. 4, 8, 12, 17 and 20). This in fact is contrary to what has been observed with iodine solutions, where the organic yield increases with decrease in iodine concentration (Table 1a). This behaviour is explained as follows. In solution, the recoil atom will react with parent compound molecule as well as solvent molecule.

In a dilute solution, the probability of interaction of recoil iodine atom with the organic compound molecule (i.e. parent molecule) is much less than its probability to react with solvent molecule and just the opposite is true with concentrated solution. Therefore, if a solution of organic compound is neutron irradiated, then the organic yield of solution would be due to solvent and solute both. The former will increase with decrease in concentration of organic compound and the later will decrease with decrease in concentration of organic compound and net effect will result in a constant value for the organic yield of solution for all concentrations. Present results support this view.
5.32 **Effect of Substituent Group on the Organic Yield of Solute**

The organic yield of pure solutes in $10^{-1}$ M solutions are compared. They decrease in the following order (Table 24).

This behaviour has been observed with all solvents, (i.e. benzene, toluene, nitrobenzene and ortho-nitrotoluene) and can be explained as follows:

$\text{NH}_2$ and $\text{OH}$ groups are electron donor and therefore would help in electrophilic substitution reaction with positively charged iodine ions. Whereas $\text{NO}_2$ group withdraws electrons from benzene ring and helps in nucleophilic substitution reaction with negatively charged iodine ions. The fact that organic yield with nitrosubstituted compounds is less, suggests that the concentration of positively charged iodine ions might be produced in larger concentration than the concentration of negatively charged iodine ions.

Therefore, one can conclude that the variation in organic yield for these compounds might be related to the ratio of concentrations of the positively and negatively
TABLE 24
ORGANIC YIELD OF SOLUTE IN $10^{-1}$M SOLUTION IN DIFFERENT SOLVENT FOR DIFFERENT COMPOUNDS

<table>
<thead>
<tr>
<th>Observation No.</th>
<th>Compound</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Nitro-benzene</th>
<th>ortho-Nitro toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PIPHNL</td>
<td>17.21</td>
<td>17.99</td>
<td>9.52</td>
<td>11.01</td>
</tr>
<tr>
<td>2</td>
<td>PINLN</td>
<td>14.41</td>
<td>13.73</td>
<td>13.44</td>
<td>7.69</td>
</tr>
<tr>
<td>3</td>
<td>OINB</td>
<td>9.97</td>
<td>12.58</td>
<td>11.08</td>
<td>11.22</td>
</tr>
<tr>
<td>4</td>
<td>PINB</td>
<td>8.58</td>
<td>14.87</td>
<td>8.71</td>
<td>8.27</td>
</tr>
<tr>
<td>5</td>
<td>2,4-DNIB</td>
<td>8.37</td>
<td>10.58</td>
<td>7.37</td>
<td>8.49</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Observation No.</th>
<th>Compounds</th>
<th>% of hot reactions</th>
<th>% of thermal reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzene</td>
<td>Toluene</td>
</tr>
<tr>
<td>1</td>
<td>orthoIodo nitro benzene</td>
<td>10.9</td>
<td>8.17</td>
</tr>
<tr>
<td>2</td>
<td>para Iodo Nitro benzene</td>
<td>6.26</td>
<td>5.91</td>
</tr>
<tr>
<td>3</td>
<td>2,4-Dinitro iodo benzene</td>
<td>5.36</td>
<td>7.24</td>
</tr>
<tr>
<td>4</td>
<td>para Iodo aniline</td>
<td>43.46</td>
<td>43.12</td>
</tr>
<tr>
<td>5</td>
<td>para Iodo phenol</td>
<td>9.15</td>
<td>14.41</td>
</tr>
</tbody>
</table>
charged iodine ions produced by the recoil reaction.

Aten has shown that iodo-compounds after (n-γ) reaction give a higher concentration of positively charged iodine ions. Therefore, it is reasonable to assume that higher organic yield with iodo phenol and para-iodo aniline is due to electrophilic substitution with positively charged iodine ions; which are produced in larger concentrations in the (n-γ) recoil reaction. The lower organic yield with other nitro compounds would be due to the presence of lower concentration of negatively charged iodine atoms. Moreover, one nitro group (either ortho or para) or two nitro groups (at ortho and para) of the benzene ring are expected to have the same effect on the nucleophilic substituting reaction with negatively charged iodine ions and thus organic yield for these nitrosubstituted compounds are expected to be the same for either mono- or dinitro-substituted compounds. This has been observed in the present experiment (Table 24).

5.33 Hot and Thermal Reactions in 10^-1 M Solution of Compounds in Different Solvents

The magnitude of hot and thermal reactions for various compounds in different solvents are shown in Table 25. Para-iodo aniline shows a very high value for hot and thermal reaction, which may be attributed to the high chemical reactivity of this compound. This fact has also been observed
by other workers that addition of aniline changes the organic yield to a large extent.

5.4 EFFECT OF TEMPERATURE ON THE ORGANIC YIELD IN SOLUTION OF 2,4-DINITROIODOBENZENE IN METHANOL AND BENZENE

These studies were made to observe the effect of temperature during neutron irradiation, on the organic yield of 2,4-dinitroiodobenzene solutions. For this purpose methanol and benzene solvents were used. The solution of this compound in methanol, on neutron irradiation with Sb/Be neutron source, shows a decrease in organic yield with increase in time of irradiation (Fig. 17). Whereas in benzene solution it remained constant. This decrease in organic yield in methanol could be due to radiolysis of solvent by gamma rays associated with the Sb/Be neutron source. Radiolysis of methanol produces H (G = 3.85), CH₃OH (G = 1.25), HCHO (G = 12.15), H₂O₂ etc. The hot recoil iodine atom produced after (n-γ) reaction may react with these radiolytic products to form a water soluble compound and would cause a decrease in organic yield. Benzene is relatively resistant to γ-radiolysis and thus show no change in organic yield in Sb/Be source at room temperature.

The effect of temperature on the organic yield of solutions was studied by using Am/Be neutron source which
is free from gamma flux. The change in organic yield with time of irradiation at different temperatures are shown in Fig. 18 and 19, for benzene and methanol solvents respectively. It is observed that methanolic solution is more sensitive to the temperature than the benzene solution. Assuming the plateau value of the organic yield in Fig. 19 (the maximum percentage of the organic yield) as $R_\infty$, $(R_\infty - R_t)$ was calculated for different temperature. Log $(R_\infty - R_t)$ versus time of irradiation was plotted, which resulted in a straight line (Fig. 20). However, due to the absence of $R_\infty$ in the benzene solution (Fig. 18) only log $R_t$ versus time of neutron irradiation was plotted which were also straight lines (Fig. 21). The slopes of these linear lines were determined and were found to be different for different temperature and not equal to the decay constant of iodine -128, suggesting that these slopes are the specific rate constant of the pseudo-first order rate kinetics. In order to get the second order specific rate constants, the above calculated pseudo-first order rate constants were divided by the concentration of the compound. The log of second order specific rate constant was then plotted against the reciprocal of irradiation temperature which showed a linear nature (Fig. 22). From the slope of these plots the activation energies for the reaction in methanol and benzene were calculated. The results are shown below.
Fig. 20: Log \( (R_\infty - R_t) \) vs. irradiation time of solution of 2,4-DNIB in methanol.
Fig. 21 - Log $R_t$ vs. irradiation time of solution of 2,4-DNIB in benzene.
Fig. 22 - Log \( k \) v/s \( 1/T \) for solution of 2,4-DNIB in methanol
<table>
<thead>
<tr>
<th>Solvents</th>
<th>Activation energy eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.17</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.49</td>
</tr>
</tbody>
</table>

The presence of plateau in methanol and its absence in benzene; low activation energy for the reaction in methanol suggests that the reaction process leading to organic yield is facilitated more in methanol than in benzene. This may be because of the presence of charged iodine ions resulting in \((n-\gamma)\) reaction. Furthermore, the organic yield in 2,4-dinitroiodobenzene is expected to be due to nucleophilic aromatic substitution reaction. A reaction of this type is expected to occur favourably in polar solvents. This argument is in agreement with the experimental observations.

5.5 THE MECHANISM OF THE PROCESS CONTROLLING THE ORGANIC YIELD IN SOLUTION

From the discussion on the results of solution of various compounds, in different solvents, the following conclusions can be drawn.

(1) After \((n-\gamma)\) recoil reaction, iodine-128 exists as either positively or negatively charged iodine ion (i.e. \(I^{\pm}\)).

(2) Major portion of the reaction occurs at hot energy level.

(3) Recoil iodine atom also reacts with solvents.
(4) Compounds studied in present work show electrophilic and nucleophilic type of substitution reactions.

(5) Cage effect has more effect in solvents which have higher intermolecular forces of attraction.

Considering these conclusions, one can draw the following general reaction mechanism responsible for giving the organic yield in the \((n-\gamma)\) reactions (\(A-I\) stands for the organic compound in the following reactions).

\[
A-I \xrightarrow{(n-\gamma)} A^0 + 128I^{\pm\delta}_{\text{hot}} \quad \cdots (1)
\]

\[
A^0 + A^0 \rightarrow [A - 128I] \quad \cdots (2)
\]

\[
A^0 + 128I^{\pm\delta}_{\text{hot}} \rightarrow [A - 128I] \quad \cdots (3)
\]

\[
[A - 127I] + 128I^{\pm\delta}_{\text{hot}} \rightarrow [A - 128I] + 127I^{\pm\delta} \quad \cdots (4)
\]

\[
128I^{\pm\delta}_{\text{hot}} + 128I^{\pm\delta}_{\text{hot}} \rightarrow 128I^{\pm\delta}_{\text{thermal}} \quad \cdots (5)
\]

\[
128I^{\pm\delta}_{\text{hot}} + \text{solvent} \rightarrow \text{Adduct product containing iodine-128} \quad \cdots (6)
\]

\[
127I_2 + 128I^{\pm\delta}_{\text{hot}} \rightarrow 127I + [127I - 128I] \quad \cdots (7)
\]

The organic yield of iodine-128 for solute can be due to reaction (3) and (4). Whereas for solvent it would be controlled by reaction (6). Reaction (2) and (5) would cause no effect on the organic yield. It is also very unlikely that there would be any considerable amount of contribution of reaction (3) on the organic yield because the products of
reaction (1) would fly off in opposite direction and probability of meeting these two components are very low. It is also obvious from the reaction (4) and (6) that the organic yield would increase with increase in concentration of organic compound (A-I). Whereas with solution containing iodine the organic yield will increase with decrease in iodine concentration because at higher concentrations of iodine, the reaction (7) will be effective and at lower concentration of iodine the organic yield will increase due to reaction (6).

5.6 KINETICS OF THERMAL ANNEALING

The correlated pair recombination model (Chapter 1.51) given by Fletcher and Brown was applied to the isothermal annealing data to calculate the activation energy and the jump frequency for the annealing process in ortho-iodonitrobenzene (OINB), para-iodonitrobenzene (PINB), 1-iodo,2,4-dinitrobenzene (2,4-DNIB), ortho-iodobenzoic acid (OIBA) and para-iodoaniline (PIANLN). According to this model

\[
\ln(R_\infty - R_t) = \ln(R_\infty - R_0) - \nu_j t
\]

where \(R_0\), \(R_t\) and \(R_\infty\) are the organic yield at zero, \(t\) and infinite time of isothermal annealing respectively, and \(\nu_j\) is the jump frequency. The jump frequency is related to the temperature by equation:

\[
\nu_j = \nu_0 e^{-E/RT}
\]
where $\nu_0$ is the typical frequency of vibration of atoms in the lattice and $E$ is the energy of activation required by the interstitial to jump to an adjacent interstitial site.

$\log (R_0 - R_t)$ versus time of isothermal annealing gave a linear plot for the various compounds (Fig. 23 to 28). From the slopes of these linear plots, the jump frequencies $\nu_j$ and from the intercepts the organic yields at zero time of annealing were calculated (Table 26). With the exception of PINB (at 383°K and 393°K) and 24 DNIB (at 348°K and 353°K) the calculated values of $R_0$ are in agreement with the experimentally observed values of $R_0$.

Furthermore $\log \nu_j$ versus reciprocal of annealing temperatures were plotted for various compounds (Fig. 29 to 31), and were found to be linear. From the slopes of these linear plots, the activation energies for the annealing process were calculated. The activation energies were found to be 0.27 eV, 1.68 eV, 1.00 eV and 1.59 eV for PINB, 24-DNIB, OIBA and PIANIN respectively. The activation energy comes out to be in the following order (Table 26).

$$\text{PINB} < \text{OIBA} < \text{PIANIN} < 24\text{-DNIB}$$

The activation energies for these organic compounds, are expected to depend upon the structural arrangements of molecules and in absence of such evidences it is not possible to explain the results. However, the structure of $p$-chloro-
<table>
<thead>
<tr>
<th>Observation No.</th>
<th>Compound</th>
<th>Annealing temperature ( T_A )</th>
<th>Intercept ( \log(E_0 - R_t) )</th>
<th>Experimental Calculated ( \log(E_0 - R_t) )</th>
<th>Jump frequency ( \log(10^4) )</th>
<th>Activation energy ( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ortho-Iodo nitro-benzene</td>
<td>318</td>
<td>0.6366</td>
<td>52.0</td>
<td>51.7</td>
<td>8.820</td>
</tr>
<tr>
<td>2</td>
<td>para-Iodo Nitro benzene</td>
<td>363</td>
<td>0.898</td>
<td>48</td>
<td>54.1</td>
<td>11.868</td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>1.286</td>
<td>48</td>
<td>56.1</td>
<td>16.880</td>
</tr>
<tr>
<td></td>
<td></td>
<td>383</td>
<td>1.210</td>
<td>48</td>
<td>61.6</td>
<td>18.528</td>
</tr>
<tr>
<td></td>
<td></td>
<td>393</td>
<td>1.1175</td>
<td>48</td>
<td>65.4</td>
<td>22.643</td>
</tr>
<tr>
<td>3</td>
<td>2,4-Dinitro-Iodo benzene</td>
<td>338</td>
<td>1.13</td>
<td>40</td>
<td>41.1</td>
<td>5.6076</td>
</tr>
<tr>
<td></td>
<td></td>
<td>343</td>
<td>1.45</td>
<td>40</td>
<td>55.1</td>
<td>8.4885</td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>1.66</td>
<td>40</td>
<td>70.3</td>
<td>15.841</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>1.67</td>
<td>40</td>
<td>70.3</td>
<td>104.99</td>
</tr>
<tr>
<td>4</td>
<td>ortho-Iodo benzoic acid</td>
<td>373</td>
<td>0.948</td>
<td>72.55</td>
<td>79.1</td>
<td>9.0535</td>
</tr>
<tr>
<td></td>
<td></td>
<td>383</td>
<td>1.082</td>
<td>72.55</td>
<td>79.2</td>
<td>16.791</td>
</tr>
<tr>
<td></td>
<td></td>
<td>393</td>
<td>1.225</td>
<td>72.55</td>
<td>76.7</td>
<td>50.891</td>
</tr>
<tr>
<td>5</td>
<td>para-Iodo aniline</td>
<td>331</td>
<td>0.76</td>
<td>36.7</td>
<td>37.3</td>
<td>11.515</td>
</tr>
</tbody>
</table>
Fig. 23 - $\log (R_\infty - R_t)$ v/s annealing time for IONB at 318°K.
Fig. 24: $\log (R_\infty - R_t)$ vs. annealing time for PINB.
Fig. 25: Log \((R_\infty - R_t)\) v/s annealing time for PINB
Fig. 26 - Log ($R_{\infty} - R_t$) vs annealing time for 2,4-DNIB
Fig. 27: \( \log (R_\infty - R_t) \) v/s annealing time for OIBA
Fig. 28 - LOG (R_\infty - R_t) v/s annealing time for PIANLN
Fig. 30 - Log $\eta_i$ v/s Reciprocal of annealing Temperature for 24-DNIB
Fig. 31  \( \log V_I \) v/s Reciprocal of annealing temperature for PIANLN
nitrobenzene is expected to be same as $p$-iodonitrobenzene. It is reported that later compound has a disordered structure. Such disorder, would certainly make the annealing process to be easier and perhaps because of this disorder, $p$-iodonitrobenzene shows the lowest activation energy. Ortho-iodobenzoic acid and para-iodoaniline, both have hydrogen bonds, and ortho-iodobenzoic acid, has two hydrogen bonds per dimer. These additional bonds, would certainly make the annealing process difficult and hence would show a higher activation energy for annealing. If 1-iodo,2,4-dinitrobenzene, is expected to follow the structure similar to nitrobenzene, then the former compound will also have a well order structure with least interstitial sites for iodine atom to migrate. Therefore, it would again need a higher activation energy for the annealing process. However, it is important to realise that in the above treatment (as suggested by Fletcher and Brown) it has been assumed that there is only one kind of recombination process occurring in the isothermal annealing and that it follows first order kinetics. Under these assumptions, the activation energies for these compounds have been calculated.

This model has been successfully applied to many other systems (i.e. inorganic compounds, organic metallic compounds and metal complex) by many workers. However, this model for the first time is applied to organic system i.e. to a molecular crystals of very low melting point. The
present treatment suggests that this model can be applied to organic solids to get thermodynamic parameters of annealing processes.

The temperature at which the isothermal annealing starts was calculated by the treatment, suggested by Maddock. $(R_{\infty} - R_0)$ versus reciprocal of annealing temperature was plotted for all compounds (Fig. 32) and the intercepts of these linear plots on the reciprocal temperature axis were determined. From these intercepts the minimum temperature at which annealing starts at the room temperature in neutron irradiated samples were calculated. These values are given in Table 27.

In the compounds studied, it is observed that with increase in melting point, the minimum temperature to start annealing, increases, which suggests that crystals with lower melting point starts annealing at relatively lower temperature. ortho-Iodobenzoic acid, however, does not follow the same trend. This may perhaps be due to the presence of dimer structure in which there are two hydrogen bonds per dimer and such structures may require a higher temperature to show the annealing. The structure of ortho-iodobenzoic acid is shown here.
### TABLE 27

**MINIMUM TEMPERATURE AT WHICH SELF ANNEALING STARTS FOR THE COMPOUNDS WHICH ARE NEUTRON IRRADIATED AT ROOM TEMPERATURE**

<table>
<thead>
<tr>
<th>Observation No.</th>
<th>Compound</th>
<th>Minimum temperature to start annealing (^{o}K)</th>
<th>Melting points of compound (^{o}K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>para Iodo aniline (PIANLN)</td>
<td>323</td>
<td>336</td>
</tr>
<tr>
<td>2</td>
<td>2,4-dinitro Iodo benzene (2,4-DNIB)</td>
<td>330.6</td>
<td>362.5</td>
</tr>
<tr>
<td>3</td>
<td>para Iodo nitro benzene (PINB)</td>
<td>341.6</td>
<td>444</td>
</tr>
<tr>
<td>4</td>
<td>ortho Iodo benzaic acid (OIBA)</td>
<td>351.5</td>
<td>435</td>
</tr>
</tbody>
</table>
Fig. 32 - Variation of $(R_\infty - R_0)$ vs. Reciprocal annealing temp.
5.7  **EFFECT OF PHASE ON ORGANIC YIELD OF VARIOUS COMPOUNDS**

The organic compounds were irradiated in a neutron source at constant temperature to a saturation value (2 hr of irradiation) and were then analysed for the organic yield. Analysis was done at room temperature. These organic yields for various compounds are plotted against the temperature of neutron irradiation (Fig. 3\(\text{a}\)). The melting point of the solids are shown in the graph. With the exception of ortho-iodobenzoic acid, all other compounds show similar trend. A sharp increase in organic yield with molten compounds may be because there is large freedom for fragmented molecules to wander around within its own molecular environment, which would facilitate a higher organic yield. Moreover, the reactivity of compound at molten state would also be high. As a result of these two factors, molten compound is expected to give highest organic yield.

If organic yield at liquid nitrogen temperature is taken as \(R_T^0\) and organic yield at any particular temperature is taken as \(R_T^{\infty}\) then a plot of \((R_T^{\infty} - R_T^0)\) versus \(1/T\) also results into a straightline. This is shown in Fig. 3\(\text{b}\). Results of ortho-iodobenzoic acid could not be included in this figure because of large range of \((R_T^{\infty} - R_T^0)\) versus \(1/T\). However, an independent plot of this compound (not shown here) gives an intercept on \(1/T\) axis at \(-84.36^\circ\text{C}\). The other organic
Fig. 32 - Variation in % organic yield with neutron irradiation temperature.
Fig. 39: $(R_{T_x} - R_{T_0})$ v/s Reciprocal of neutron irradiation temperature for different compounds.
compounds show an intercept at different temperatures as shown below. These intercepts may be taken as the starting of self annealing temperature for the respective organic compounds.

- OINB: 30°C
- PIANLN: 27.7°C
- PINB: 18°C
- 24DNIB: 16°C
- OIBA: -34.86°C

This shows that, with the exception of ortho-iodo-benzoic acid, all compounds start annealing at around room temperature. If this be so, then the linear horizontal plot of Fig. 3g should have been a non-horizontal and the organic yield at liquid nitrogen temperature should have been lower than organic yield at room temperature. This discrepancy may be because of analytical technique followed in this work. The liquid nitrogen temperature irradiated samples after removal from the neutron source were analysed at room temperature. During this process, annealing may have occurred to show an organic yield similar to that obtained at the room temperature. Had the analysis been done at liquid nitrogen, one could have obtained a different trend in the self annealing graph - a fact which is worth pursuing further. ortho-Benzoic acid behaves very differently and
unless one has TGA/DTA, data it is difficult to interpret its results, because it may have some phase changes in the structure.

5.8 THE MECHANISM OF ISOTHERMAL ANNEALING

In the molecular compounds, the migration of large (bulky) organic fragments in the crystal lattice is very difficult. On the other hand, iodine ions/atoms can migrate through the interstitial sites easily. These halide ions would be trapped at the interstitial sites, which on heating would either react with neighbouring fragmented organic molecule or would wander through the interstitial space till it finds a fragmented organic molecule for the reaction. A reaction of a later type would lead to an organic yield. However, if iodine interacts with its own molecules i.e., iodine atom/ions then there would be no contribution towards an organic yield. Therefore, it is reasonable to assume that in a molecular crystal most of the fragments formed after (n-Y) reaction would remain intact at the sites of their formation, and would most probably react with their neighbouring compounds. Only a few percentage of iodine atoms/ions, which have migrated out of the neighbouring organic fragmented molecules, would show isothermal annealing at higher temperature. It is for these reasons that initial organic yield with these compounds are as high as 70%
(Table 26) and the extent of annealing is only about 10% to 20% of the initial organic yield. The higher activation energies for the annealing process of all these compounds are expected to be related to the structure of these compounds, as suggested earlier.